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Steric effect of allyl substituent on the molecular structures of allyltitanium complexes

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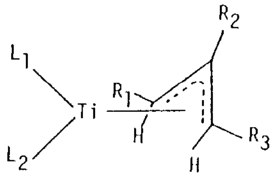
Abstract

The crystal structures of a series of allyltitanium complexes have been determined by X-ray crystallography. Crystals of $(C_5H_5)_2Ti$(1,3-dimethylallyl) (**1**) are monoclinic, space group $P2_1/n$, with $a = 13.353(2)$, $b = 7.674(1)$, $c = 25.543(2)$ Å, $\beta = 90.92(1)°$, and $Z = 8$. Crystals of $(C_5H_5)_2Ti$(2-methylallyl) (**2**) are orthorhombic, space group *Pbca*, with $a = 15.299(4)$, $b = 25.797(2)$, $c = 12.014(1)$ Å, and $Z = 16$. The unit cells of **1** and **2** each contain two molecules in a crystallographic asymmetric unit. The coordination geometry of a non-substituted allyltitanium compound was determined for $(C_5H_5)(C_5Me_5)$-Ti(allyl) (**3**) with the mixed ancillary ligands since $(C_5H_5)_2Ti$(allyl) (**4**) includes the packing disorder. Crystals of **3** are orthorhombic, space group *Pnma*, with $a = 9.633(1)$, $b = 12.743(1)$, $c = 12.718(1)$ Å, and $Z = 4$. The molecular structure exhibits a crystallographic mirror symmetry. All the crystal structures were refined by the full-matrix least-squares to the R indices of 0.062, 0.051, and 0.065 for **1**, **2**, and **3**, respectively. The allyl groups are η^3-coordinated to the metal with a mirror symmetry. Detailed comparisons of these complexes revealed the remarkable steric effect by the methyl substituents of the allyl ligands on the coordination geometries of allyl ligands to titanium atom. Complex **1** has the longest Ti–C(1) and Ti–C(3) bonds, while complex **2** has the longest Ti–C(2) bond. The shortest Ti–allyl bonds were seen in complex **3**.

Introduction

Allyltitanium compounds are known to serve either as a key intermediate or as an efficient synthetic reagent in the Ziegler–Natta polymerization of conjugated dienes [1], the stereoselective oligomerization of conjugated dienes [2], the isomerization of olefins [3], and the stereoselective synthesis of a variety of homoallyl alcohols [4] and their analogues [5]. In spite of their important role and diverse utility, the stereochemistry of the allyltitanium compounds, especially those of low valent (η^3-allyl)Ti^{III} species, has not been well established, except for Cp_2Ti(1,2-dimethylallyl) [6], due to their paramagnetic nature and the difficulty in handling these compounds. Here we present the systematic X-ray work performed on a series of substituted and unsubstituted allyltitanium(III) compounds of the type $(C_5R_5)_2$-Ti(CHRCRCHR) so as to elucidate their exact stereochemical disposition (η^1- and η^3-coordination), the geometries (*syn* and *anti*) of ligated allyl group and the effect of the substituent on the mode of bonding. Detailed comparison of the present data with those of the conventional allyl complexes of the late transition metals (Pt, Pd, Ni, etc.) confirmed the remarkable structural features ascribable to the enhanced M–C σ-bonding character of the early transition metal-allyl complexes.

The samples employed in this work (**1**–**6**) were prepared either by the reaction of allyl Grignard reagent with $(C_5H_5)_2TiCl_2$ or by the hydrotitanation of the conjugated dienes.



	L_1	L_2	R_1	R_2	R_3
1	Cp	Cp	Me	H	Me
2	Cp	Cp	H	Me	H
3	Cp	Cp*	H	H	H
4	Cp	Cp	H	H	H
5	Cp	Cp	Me	Me	H
6	Cp	Cp	Me	H	H

Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5

Experimental

Preparation of $Ti(C_5H_5)(C_5Me_5)Cl_2$. The starting material $(C_5Me_5)TiCl_3$ was prepared by the 1 : 1 reaction of $TiCl_4$ with $(C_5Me_5)SiMe_3$ in hexane at 60 °C as described previously [2]. To a stirred solution of $(C_5Me_5)TiCl_3$ (5.8 g, 20 mmol) in THF (200 mL) was added dropwise a solution of $Na(C_5H_5)$ (1.76 g, 20 mmol) in THF (30 mL) at 0 °C. The solution turned from red–orange to purple during the addition. After the solution had been stirred for 1 h at ambient temperature, the solvent was evaporated to dryness, the residue was extracted with $CHCl_3$ (200 mL), and filtered to separate the salt. Concentration and cooling of the extracts to −20 °C gave $(C_5H_5)(C_5Me_5)TiCl_2$ as red–purple crystals in 82% yield. Anal. Found: C, 56.33; H, 6.32. $C_{15}H_{20}Cl_2Ti$ calc.: C, 56.46; H, 6.32. ^1H NMR ($CDCl_3$): 6.24 (s, 5H, C_5H_5), 2.20 (s, 15H, C_5Me_5) ppm.

Preparation of $(C_5H_5)_2Ti$(1,3-dimethylallyl) (1) and $(C_5H_5)_2Ti$(1,2-dimethylallyl) (5). These complexes were prepared with some modification of Martin's method [6]. Typical procedure is as follows. To a THF solution (30 mL) of $(C_5H_5)_2TiCl_2$ (0.5 g, 2 mmol) was added a solution of isoprene (0.27 g, 4 mmol) in THF (5 mL). An ethereal solution of ^iPrMgCl (2.5 *M*, 1.6 mL 4 mmol) was added dropwise to the mixture with vigorous stirring at 0 °C. The solution turned from red to purple immediately after the addition. The mixture was stirred at ambient temperature for 15 min, and then evaporated to dryness. The residue was extracted with 40 mL of hexane at 60 °C. After the removal of salts by centrifugation, the solution was concentrated and cooled to −20 °C to give $(C_5H_5)_2Ti$(1,2-dimethylallyl) (**5**) in 84%

yield as purple crystals. Repeated crystallization in hexane at −20 °C yielded single crystals suitable for the X-ray diffraction study.

Preparation of $(C_5H_5)_2$Ti(2-methylallyl) (2), $(C_5H_5)(C_5Me_5)$Ti(allyl) (3), $(C_5H_5)_2$Ti(allyl) (4), and $(C_5H_5)_2$Ti(1-methylallyl) (6). These compounds were synthesized by the reaction between $(C_5H_5)_2TiCl_2$ and the corresponding Grignard reagents with some modification of the procedure reported by Martin and Jellinek [7]. Solvents were thoroughly dried over Na/K alloy, degassed and then distilled before use. Typically, complex **3** was prepared as follows. The starting allylmagnesium compounds were prepared from 3-bromo-1-propene. A solution of allylmagnesium bromide (5 mmol) in diethyl ether (10 mL) was added dropwise to a solution of $(C_5H_5)(C_5Me_5)TiCl_2$ (0.8 g, 2.5 mmol) in THF (30 mL) with magnetic stirring at 0 °C. After 30 min stirring at ambient temperature the solvent was evaporated to dryness in vacuo, hexane (40 mL) was added, and the resulting mixture was heated to 60 °C for 10 min in order to separate the magnesium salt. Residual colloidal salts were then completely removed by centrifugation under Ar. Concentration and cooling of the hexane extracts gave $(C_5H_5)(C_5Me_5)$Ti(allyl) (**3**) as purple crystals in 76% yield.

The complexes **2**, **4**, and **6** were obtained similarly starting from $(C_5H_5)_2TiCl_2$ and the appropriate Grignard reagents.

*X-Ray crystallography of **1**, **2**, **3**, and **4**.* The air-sensitive crystals of **1**, **2**, **3**, and **4** were sealed in a thin-walled glass capillary tube under argon. All the X-ray diffraction studies were carried out at 20 °C on a Rigaku automated four-circle diffractometer with graphite-monochromatized Mo-K_α radiation. The unit cell parameters were determined by a least-squares fit to the 2θ values of 25 strong high-angle reflections. The crystal data and experimental conditions for **1**, **2**, and **3** are summarized in Table 1. No significant intensity decay of the standard reflections was observed during the data collection. The intensity data were corrected for the usual Lorentz and polarization effects but not for absorption because of the small μ values. The crystal structures were solved by the conventional heavy-atom method and were refined by full-matrix least-squares using XRAY-76 [8] including the observed reflections $[|F_o| > 3\sigma(F_o)]$. After the anisotropic refinement of the non-hydrogen atoms, all the hydrogen atoms were located in the difference Fourier maps with help of geometrical calculations and were refined isotropically. The crystal structure analyses of $(\eta^5\text{-}C_5H_5)_2$Ti(allyl) (**4**) and $(\eta^5\text{-}C_5H_5)_2$Ti(1-methylallyl) (**6**) have been tried extensively. However, both crystals include marked rotational disorder in the cyclopentadienyl ligands which prevented the elucidation of the accurate molecular structure [9*]. The crystallization of **5** to isolate crystals other than the twinned one reported [6] has also been tried [9*].

All the calculations were carried out on an ACOS 930 computer system at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Results and discussion

Molecular structure of $(C_5H_5)_2$Ti(1,3-dimethylallyl) (1). The crystal lattice of complex **1** includes two crystallographically independent molecules in the asymmet-

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Crystal data and summary of data collection and structure refinement

	1	**2**	**3**
Allyl ligand	1,3-dimethylallyl	2-methylallyl	allyl
Formula	$C_{15}H_{19}Ti$	$C_{14}H_{17}Ti$	$C_{18}H_{25}Ti$
FW	247.2	233.2	289.2
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$	*Pbca*	*Pnma*
Temp., °C	20	20	20
a, Å [a]	13.353(2)	15.299(4)	9.633(1)
b, Å	7.674(1)	25.797(2)	12.743(1)
c, Å	25.543(2)	12.014(1)	12.718(1)
β, deg	90.92(1)		
V, Å^3	2617.2(6)	4742(1)	1561.2(3)
Z	8	16	4
D_{calcd}, g cm^{-3}	1.254	1.306	1.231
$F(000)$	1048	1968	620
μ(Mo-K_α)	6.4	7.0	5.5
Crystal size, mm	$0.50\times0.40\times0.30$	$0.50\times0.35\times0.30$	$0.55\times0.30\times0.25$
2θ range, deg [b]	$4<2\theta<60$	$4<2\theta<60$	$4<2\theta<60$
Scan speed, deg min^{-1} in 2θ	4.0	4.0	4.0
Scan width, deg in 2θ	$2.0+0.70\tan\theta$	$2.0+0.70\tan\theta$	$2.0+0.70\tan\theta$
Background, s	5	5	5
Range of h, k, l	±17, +9, +35	+21, +36, +16	+13, +17, +17
Decay for irradiation in F [c]	−8%	<1%	<1%
Reflections measured	7266	6899	2372
Reflections observed [d]	5730	5333	1627
No. of variables	442	402	147
GOF [e]	1.021	1.027	1.029
R [f]	0.062	0.051	0.065
R_w [g]	0.089	0.074	0.097

[a] Least-squares refinement of the 2θ values for 25 reflections with $2\theta > 25°$. [b] Intensity data were collected on a Rigaku four-circle diffractometer using graphite-monochromatized Mo-K_α radiation by the θ–2θ scan method. [c] Damage correction was applied for **1**. [d] $|F_o| > 3\sigma(F_o)$. [e] $\Sigma w(|F_o| - |F_c|)^2/(n-m)$, where n and m are the number of reflections used and variables refined, respectively. [f] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [g] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$, and $g = 0.003$ for all the complexes.

ric unit. Their final atomic coordinates for non-hydrogen atoms are listed in Table 2, and the important interatomic bond distances and angles are in Table 3. Comparison of the structural parameters between the two independent molecules (**1**-1 and **1**-2), revealed virtually identical structure. In Fig. 1 is depicted an ORTEP drawing of one of the two molecules of **1**, which clearly shows the presence of an approximate mirror symmetry in the molecule. The 1,3-dimethylallyl ligand assumes planar *cis–syn* geometry and shows η^3-coordination to the metal. Two cyclopentadienyl ligands assume a staggered configuration to release the steric repulsion between them. In addition, one of the cyclopentadienyl ligands takes up a position so as to minimize steric interaction by locating the C(21)–C(25) bond nearly parallel to the allyl C(1) $\cdots$ C(3) interatomic axis, while the C(11)–C(12) bond in the other cyclopentadienyl ligand is oriented so that C(11) atom fills the space under C(2).

Table 2

Fractional atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in $(\eta^5\text{-}C_5H_5)_2$Ti(1,3-dimethylallyl) (**1**) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Molecule 1				
Ti	0.10275(4)	0.04911(6)	−0.14182(3)	3.07
C(1)	0.0937(3)	0.3221(5)	−0.1900(2)	4.9
C(2)	0.0737(3)	0.3543(4)	−0.1378(2)	4.6
C(3)	0.1343(4)	0.3149(5)	−0.0946(2)	5.4
C(4)	0.0203(4)	0.3695(7)	−0.2330(2)	7.1
C(6)	0.1003(5)	0.3518(8)	−0.0394(2)	8.2
C(11)	0.2764(3)	0.0771(7)	−0.1621(3)	7.2
C(12)	0.2298(4)	−0.0156(8)	−0.2037(3)	7.3
C(13)	0.1972(4)	−0.1761(6)	−0.1823(3)	7.4
C(14)	0.2230(4)	−0.1778(7)	−0.1287(3)	7.2
C(15)	0.2714(3)	−0.0254(70	−0.1163(3)	7.2
C(21)	−0.0767(3)	0.0446(6)	−0.1521(2)	5.6
C(22)	−0.0390(3)	−0.1188(7)	−0.1669(2)	6.1
C(23)	0.0027(3)	−0.1953(5)	−0.1225(3)	6.6
C(24)	−0.0077(4)	−0.0786(7)	−0.0807(2)	6.3
C(25)	−0.0573(3)	0.0670(5)	−0.1000(2)	5.6
Molecule 2				
Ti	0.39915(4)	0.44743(6)	0.10877(3)	3.14
C(1)	0.2634(3)	0.5402(5)	0.1617(2)	4.7
C(2)	0.2672(3)	0.6526(5)	0.1193(2)	4.1
C(3)	0.2629(3)	0.6044(5)	0.0663(2)	4.2
C(4)	0.2755(4)	0.606(1)	0.2171(2)	6.7
C(6)	0.2712(3)	0.7363(5)	0.0229(2)	5.4
C(11)	0.2904(3)	0.2026(5)	0.0925(2)	5.2
C(12)	0.3525(4)	0.1595(5)	0.1363(2)	5.4
C(13)	0.4513(3)	0.1510(4)	0.1200(2)	5.1
C(14)	0.4505(3)	0.1862(4)	0.0655(2)	5.1
C(15)	0.3521(4)	0.2189(5)	0.0487(2)	5.1
C(21)	0.4827(3)	0.6993(5)	0.1465(2)	5.2
C(22)	0.5313(4)	0.5500(6)	0.1643(3)	6.7
C(23)	0.5742(3)	0.4719(5)	0.1202(3)	7.9
C(24)	0.5484(4)	0.5710(6)	0.0762(3)	6.6
C(25)	0.4936(3)	0.7103(5)	0.0927(2)	5.4

The coordination geometries around titanium atom are listed in Table 4 together with those found in the complexes **2** and **3**. The Ti atom has a distorted tetrahedral geometry if the terminal carbons of the allyl group are regarded as occupying two coordination sites. The angles, ϕ_1, defined by CCP1, Ti, and CCP2, are 132.4° and 132.7°, respectively for **1**-1 and **1**-2. The angles ϕ_2, defined by CCP1, Ti, and M1 (110.5° and 110.8°) and the angles ϕ_3, defined by CCP2, Ti, and M1 (117.1° and 116.5°) are much smaller than ϕ_1. The sum of ϕ_1, ϕ_2 and ϕ_3 is exactly 360° indicating that the vectors connecting the Ti atom with CCP1, CCP2 and M1 are in one plane. The coordination geometries of the ligand around the titanium atom can be related to the angles γ, δ, and ϵ. The δ values are around 91–100° in the **1**–**3** complex. One of the important structural features of **1** is a relatively long titanium–terminal carbon bonds (2.432 and 2.404 Å for **1**-1, 2.388 and 2.424 Å for **1**-2) as

Table 3

Interatomic bond distances (Å) and angles (deg) for non-hydrogen atoms in (η^5-C_5H_5)$_2$Ti(1,3-dimethylallyl) (**1**) with estimated standard deviations in parentheses

	Molecule 1	Molecule 2
(a) Bond distance		
Ti–C(1)	2.432(4)	2.388(4)
Ti–C(2)	2.376(4)	2.382(3)
Ti–C(3)	2.404(4)	2.424(3)
Ti–C(11)	2.394(7)	2.407(4)
Ti–C(12)	2.390(5)	2.404(5)
Ti–C(13)	2.384(6)	2.395(4)
Ti–C(14)	2.389(6)	2.395(4)
Ti–C(15)	2.404(6)	2.407(4)
Ti–C(21)	2.406(5)	2.424(4)
Ti–C(22)	2.370(5)	2.381(5)
Ti–C(23)	2.359(6)	2.359(7)
Ti–C(24)	2.376(5)	2.370(6)
Ti–C(25)	2.408(5)	2.418(5)
C(1)–C(2)	1.385(5)	1.387(5)
C(1)–C(4)	1.505(6)	1.509(6)
C(2)–C(3)	1.392(6)	1.404(5)
C(3)–C(6)	1.514(7)	1.507(5)
C(11)–C(12)	1.414(9)	1.422(6)
C(11)–C(15)	1.414(9)	1.405(6)
C(12)–C(13)	1.419(8)	1.392(6)
C(13)–C(14)	1.407(9)	1.417(6)
C(14)–C(15)	1.372(9)	1.399(6)
C(21)–C(22)	1.405(7)	1.390(7)
C(21)–C(25)	1.362(7)	1.387(6)
C(22)–C(23)	1.388(8)	1.407(9)
C(23)–C(24)	1.402(8)	1.396(9)
C(24)–C(25)	1.386(7)	1.366(7)
(b) Bond angle		
C(1)–Ti–C(3)	62.0(1)	62.3(1)
C(2)–C(1)–C(4)	121.8(4)	121.2(3)
C(1)–C(2)–C(3)	127.4(4)	126.1(3)
C(2)–C(3)–C(6)	121.3(4)	122.1(3)
C(12)–C(11)–C(15)	108.5(5)	107.8(4)
C(11)–C(12)–C(13)	106.3(5)	108.6(4)
C(12)–C(13)–C(14)	108.2(5)	107.0(4)
C(13)–C(14)–C(15)	108.9(6)	109.2(4)
C(11)–C(15)–C(14)	108.1(6)	107.4(4)
C(22)–C(21)–C(25)	108.2(4)	108.5(4)
C(21)–C(22)–C(23)	107.4(5)	106.5(5)
C(22)–C(23)–C(24)	108.0(5)	108.3(6)
C(23)–C(24)–C(25)	107.2(5)	107.7(5)
C(21)–C(25)–C(24)	109.2(4)	108.9(4)

compared with the corresponding distances in complexes **2** and **3** due to substitution on both C(1) and C(3) carbons. Thus, the titanium–central carbon bond of **1** (2.376 Å for **1**-1 and 2.382 Å for **1**-2) are significantly shorter than the titanium–terminal carbon bonds. The substitution effect is also seen in the C(1) ··· C(3) interatomic distance in **1**, the distance (av. 2.488 Å) being longest in **1**–**3**. However, the bite

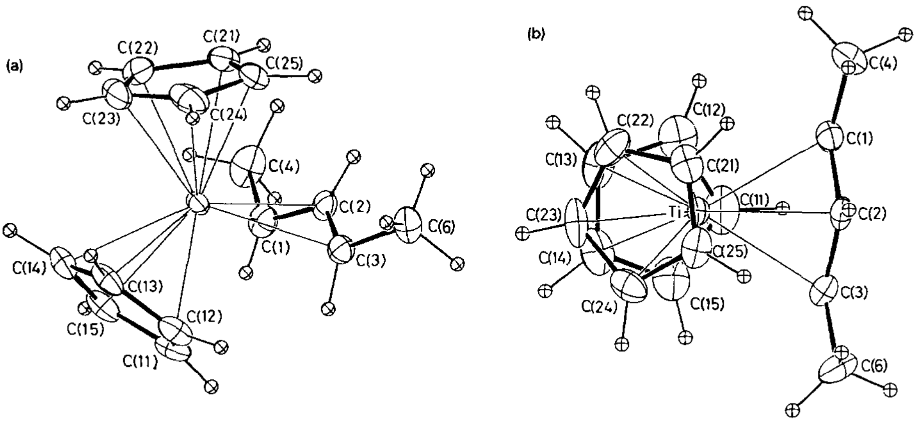


Fig. 1. Molecular structure of $(C_5H_5)_2Ti$(1,3-dimethylallyl) (**1**) by the ORTEP drawing with the thermal ellipsoids at 20% probability level; (a) side view, and (b) top view.

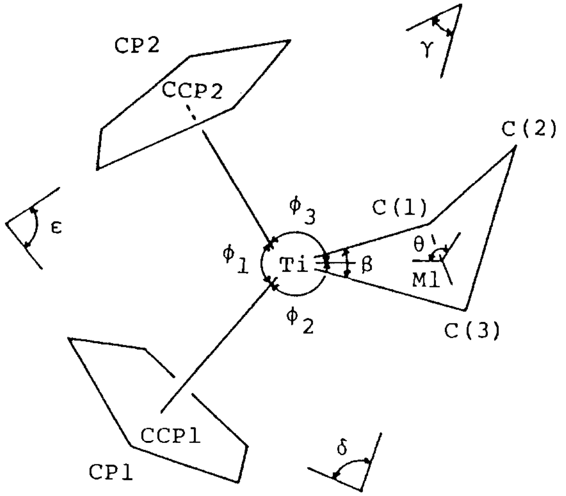
angle, β, defined by allyl ligand and titanium atom (62.0 and 62.2° respectively, in each molecule) becomes comparable with those in the complexes **2** and **3** as a result of the cancelling effect by the relatively long Ti–C(1) and Ti–C(3) distances. This feature is reflected in the dihedral angle, θ, defined by the plane composed of the Ti, C(1), and C(3) atoms and the plane of the, C(1), C(2), and C(3) atoms (112.3 and 113.3° respectively in each molecule), its value being smallest among the complexes **1**–**3**. The C(1)–C(2) distances (1.385 Å for **1**-1 and 1.387 Å for **1**-2) are analogous to the C(2)–C(3) distances (1.392 Å for **1**-1 and 1.404 Å for **1**-2) in accord with the observation of an approximate mirror symmetry in the molecule. Thus, contribution by the σ,η^1-limiting structure is negligible in complex **1**. The observed C–C bond distances are nearly the same as those reported for a Zr complex (1.380 Å and 1.388 Å, Zr^1 in Ref. 10).

Molecular structure of $(C_5H_5)_2Ti$(2-methylallyl) (2). The steric effect of the alkyl substitution at the central allyl carbon is examined here. The crystal lattice of the complex **2** also includes two crystallographically independent molecules (**2**-**1** and **2**-**2**) in the asymmetric unit. The final atomic coordinates for the non-hydrogen atoms in complex **2** are listed in Table 5, and selected interatomic bond distances and angles in Table 6. The two independent molecules in the unit cell are assumed to have essentially the same molecular structure. The ORTEP drawing of one of the two molecules is depicted in Fig. 2, which also shows the approximate mirror symmetry in the molecule.

The effect of alkyl substitution at the central carbon of allyl ligand is reflected in the elongated Ti–C(2) distances (2.464 and 2.451 Å for **2**-1 and **2**-2); i.e. these values are ca. 0.07 Å greater than the Ti–C(1) and Ti–C(3) distances in **2** and ca. 0.1 Å longer than that in the non-substituted allyl compound **3**. Hence the Ti–M1 distances (2.045 and 2.046 Å) are slightly shorter than those in complex **1**. Since the methyl substituent on C(2) is turned away from the metal, the bent angles (θ) in complex **2** (121.5 and 120.2°) are the largest of those observed for the complexes described here. In Table 7 are listed the non-bonded atomic contacts between C_5H_5 or C_5Me_5 and allyl ligands for **1**–**3**. The contact distances between C(4) or C(6) in 1,3-dimethylallyl and C(21) or C(25) in Cp2 ligand [C(21–C(25)] are in a range of

Table 4

Coordination geometry around the titanium atom in allyltitanium complexes



	1-1	**1-2**	**2-1**	**2-2**	**3**
Ti–CCP1 [a], Å	2.072	2.082	2.088	2.090	2.094
Ti–CCP2, Å	2.071	2.078	2.070	2.066	2.083
Ti–M1 [b], Å	2.073	2.059	2.045	2.046	2.033
C(1) ··· C(3), Å	2.489	2.487	2.458	2.446	2.469
β [c], deg	62.0	62.2	62.0	61.7	62.5
θ [d], deg	112.3	113.3	121.5	120.2	114.7
ϕ_1 [e], deg	132.4	132.7	131.5	131.4	132.7
ϕ_2, deg	110.5	110.8	111.1	111.0	113.3
ϕ_3, deg	117.1	116.5	117.4	117.6	114.0
γ [f], deg	38.9	38.0	30.0	30.9	39.2
δ [f], deg	91.6	92.1	100.2	99.5	91.5
ϵ [f], deg	49.6	49.9	49.8	49.6	49.4
C(1)–C(2)–C(3), deg	127.4	126.1	122.6	122.8	126.7
Ti–C(1), Å	2.432	2.388	2.395	2.367	2.379
Ti–C(2), Å	2.376	2.382	2.464	2.451	2.360
Ti–C(3), Å	2.404	2.424	2.378	2.400	2.379
C(1)–C(2), Å	1.385	1.387	1.410	1.403	1.381
C(2)–C(3), Å	1.392	1.404	1.392	1.383	1.381

[a] CCP: centroid of cyclopentadienyl ligand. [b] M1: midpoint of C(1) and C(3). [c] β: bite angle, C(1)–Ti–C(3). [d] θ: bent angle between the planes composed of C(1), Ti, and C(3) atoms and of C(1), C(2), and C(3) atoms. [e] ϕ_{1-3}: angles formed by the bonds between CCP1, CCP2, M1, and Ti. [f] γ, δ, ϵ: angles formed by the planes of two cyclopentadienyl and allyl ligands.

3.392–3.500 Å, while those between C(5) in 2-methylallyl ligand and C(21) or C(25) are rather short, between 3.152 and 3.265 Å. Therefore, the non-bonded repulsion between the C(5) in 2-methylallyl and Cp2 ligands is regarded as being very important in determining the coordination geometry of allyl ligand to titanium atom. The large variation of these values, however, little affects the angles ϕ_1, ϕ_2 and ϕ_3. The unique disposition of the 2-methylallyl ligand makes γ the smallest

Table 5

Fractional atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in (η^5-C_5H_5)$_2$Ti(2-methylallyl) (**2**) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Molecule 1				
Ti	0.08684(3)	0.23920(2)	0.07416(4)	2.66
C(1)	0.0013(2)	0.3110(2)	0.0103(3)	4.1
C(1)	−0.0046(2)	0.3139(2)	0.1272(3)	3.7
C(3)	0.0684(2)	0.3109(2)	0.1962(3)	3.6
C(5)	−0.0935(3)	0.3125(2)	0.1813(4)	5.6
C(11)	0.2020(2)	0.2908(2)	0.0041(3)	4.2
C(12)	0.1826(3)	0.2562(2)	−0.0807(3)	4.3
C(13)	0.2006(3)	0.2062(2)	−0.0433(3)	4.8
C(14)	0.2355(3)	0.2097(2)	0.0643(4)	5.4
C(15)	0.2381(2)	0.2618(2)	0.0942(3)	5.0
C(21)	−0.0535(3)	0.1978(2)	0.0936(4)	5.4
C(22)	−0.0027(3)	0.1677(2)	0.0214(3)	5.3
C(23)	0.0676(3)	0.1480(2)	0.0821(4)	5.5
C(24)	0.0612(3)	0.1669(2)	0.1908(3)	5.6
C(25)	−0.0131(3)	0.1970(2)	0.1983(3)	5.2
Molecule 2				
Ti	0.13806(3)	0.50469(2)	0.18402(4)	2.71
C(1)	0.1523(2)	0.4356(2)	0.0556(3)	3.8
C(I)	0.2266(2)	0.4308(2)	0.1231(3)	3.8
C(3)	0.2226(3)	0.4305(2)	0.2381(3)	4.5
C(5)	0.3156(3)	0.4326(2)	0.0653(4)	5.5
C(11)	0.0319(3)	0.5340(2)	0.3185(3)	4.6
C(12)	0.0475(3)	0.4819(2)	0.3422(3)	4.8
C(13)	0.0189(3)	0.4528(2)	0.2493(4)	4.7
C(14)	−0.0154(2)	0.4870(2)	0.1701(3)	4.7
C(15)	−0.0074(2)	0.5373(2)	0.2136(3)	4.7
C(21)	0.2324(3)	0.5490(2)	0.0553(3)	5.0
C(22)	0.1585(3)	0.5796(2)	0.0721(3)	4.9
C(23)	0.1590(3)	0.5955(2)	0.1828(4)	5.2
C(24)	0.2321(3)	0.5736(2)	0.2355(3)	5.3
C(25)	0.2777(3)	0.5451(2)	0.1555(3)	4.9

value and δ the largest, while the ϵ values are virtually identical with those for **1** and **3**.

Molecular structure of (C_5H_5)(C_5Me_5)Ti(allyl) (3). Since the repeated X-ray work on (C_5H_5)$_2$Ti(allyl) (**4**) revealed the somewhat fluxional coordination properties of the cyclopentadienyl as well as the allyl ligands, the compound (C_5H_5)(C_5Me_5)Ti(allyl) (**3**) with mixed ancillary ligands was synthesized to apply the structural analysis of non-substituted allyl compounds. Complex **3** shows no fluxionality and provides sufficient structural information. The molecule involves a crystallographic mirror symmetry, which passes through the titanium atom, the central C(2) carbon of the allyl ligand, and the centers of gravity of the two cyclopentadienyl ligands. The final atomic coordinates for non-hydrogen atoms are listed in Table 8, and selected interatomic bond distances and angles in Table 9. The molecular structure is depicted in Fig. 3 as an ORTEP drawing. The coordination geometry of **3** is

Table 6

Interatomic bond distances (Å) and angles (deg) for non-hydrogen atoms in (η^5-C_5H_5)$_2$Ti(2-methylallyl) (**2**) with estimated standard deviations in parentheses

(a) Bond distance		
Ti–C(1)	2.395(3)	2.367(6)
Ti–C(2)	2.464(3)	2.451(6)
Ti–C(3)	2.378(3)	2.400(6)
Ti–C(11)	2.409(3)	2.412(6)
Ti–C(12)	2.408(3)	2.424(6)
Ti–C(13)	2.397(4)	2.394(6)
Ti–C(14)	2.401(4)	2.397(6)
Ti–C(15)	2.399(4)	2.405(6)
Ti–C(21)	2.410(4)	2.405(6)
Ti–C(22)	2.383(4)	2.376(6)
Ti–C(23)	2.374(4)	2.364(6)
Ti–C(24)	2.366(4)	2.370(6)
Ti–C(25)	2.398(4)	2.401(6)
C(1)–C(2)	1.410(4)	1.403(4)
C(2)–C(3)	1.392(4)	1.383(4)
C(2)–C(5)	1.508(5)	1.529(5)
C(11)–C(12)	1.401(5)	1.394(5)
C(11)–C(15)	1.405(5)	1.399(5)
C(12)–C(13)	1.392(5)	1.413(5)
C(13)–C(14)	1.401(5)	1.399(5)
C(14)–C(15)	1.390(6)	1.404(5)
C(21)–C(22)	1.400(6)	1.393(5)
C(21)–C(25)	1.402(6)	1.394(5)
C(22)–C(23)	1.396(6)	1.392(5)
C(23)–C(24)	1.398(6)	1.403(6)
C(24)–C(25)	1.380(6)	1.398(5)
(b) Bond angle		
C(1)–Ti–C(3)	62.0(1)	61.7(2)
C(1)–C(2)–C(3)	122.6(3)	122.8(3)
C(1)–C(2)–C(5)	119.0(3)	117.2(3)
C(3)–C(2)–C(5)	117.8(3)	119.6(3)
C(12)–C(11)–C(15)	108.0(3)	108.4(3)
C(11)–C(12)–C(13)	107.8(3)	107.3(3)
C(12)–C(13)–C(14)	108.2(3)	108.6(3)
C(13)–C(14)–C(15)	108.2(3)	107.3(3)
C(11)–C(15)–C(14)	107.8(3)	108.4(3)
C(22)–C(21)–C(25)	107.7(4)	108.6(3)
C(21)–C(22)–C(23)	107.8(4)	107.5(3)
C(22)–C(23)–C(24)	107.9(4)	108.5(3)
C(23)–C(24)–C(25)	108.4(4)	107.4(3)
C(21)–C(25)–C(24)	108.2(4)	107.9(3)

analogous to those found in **1** in spite of the absence of substituents at the C(1) and C(3) positions. The C(2) carbon of the allyl group points away from bulky pentamethylcyclopentadienyl group to minimize the steric interaction of the allyl C(2) carbon with C(11) and C(16) in the C_5Me_5 ligand. Such a steric effect as observed between the C_5Me_5 and allyl ligand was also seen in a series of titanium-diene complexes of type (C_5Me_5)TiCl(diene). The preference for *supine* and *prone*

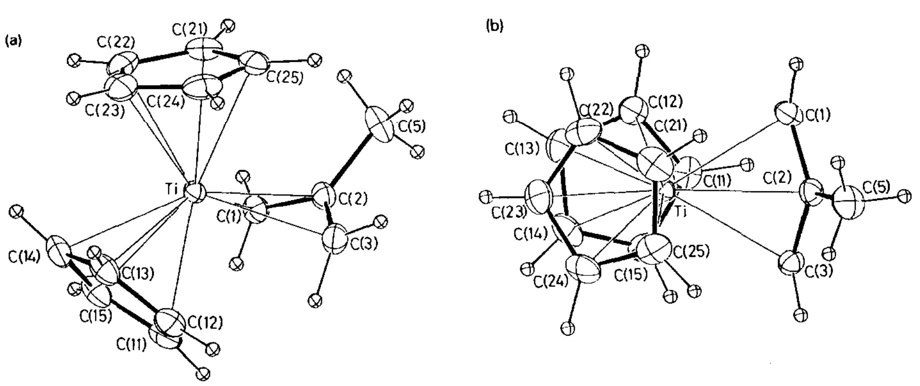


Fig. 2. Molecular structure of $(C_5H_5)_2Ti$(2-methylallyl) (**2**) by the ORTEP drawing with the thermal ellipsoids at 20% probability level; (a) side view, and (b) top view.

Table 7

Nonbonded short contacts (Å) between (η^5-C_5H_5)/(η^5-C_5Me_5) and allyl ligands

		1-1	**1-2**	**2-1**	**2-2**	**3**
C(1)	··· C(11)	3.153	3.161	3.175	3.128	3.225
	··· C(12)	3.188	3.224	3.300	3.199	3.254
	··· C(21)	3.273	3.201	3.201	3.172	3.124
C(2)	··· C(11)	3.505	3.535	3.594	3.567	3.589
	··· C(21)	3.129	2.971	3.113	3.158	2.958
	··· C(25)	2.985	3.141	3.136	3.074	
C(3)	··· C(11)	3.165	3.175	3.166	3.172	
	··· C(15)	3.243	3.223	3.139	3.241	
	··· C(25)	3.189	3.246	3.192	3.230	
C(4)	··· C(21)	3.500	3.401			
C(5)	··· C(21)			3.201	3.265	
	··· C(25)			3.230	3.152	
C(6)	··· C(25)	3.392	3.446			

Table 8

Fractional atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in (η^5-C_5H_5)(η^5-C_5Me_5)Ti(allyl) (**3**) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Ti	0.1209(1)	0.2500(0)	−0.00522(6)	3.26
C(1)	0.202(1)	0.153(1)	−0.1528(5)	7.4
C(2)	0.158(2)	0.2500(0)	−0.1886(6)	7.7
C(11)	0.3630(6)	0.2500(0)	0.0472(6)	3.5
C(12)	0.2992(6)	0.1597(6)	0.0921(5)	3.3
C(13)	0.2001(6)	0.1946(6)	0.1666(6)	3.3
C(16)	0.4927(5)	0.2500(0)	−0.0187(4)	5.6
C(17)	0.3422(4)	0.0466(3)	0.0746(3)	4.9
C(18)	0.1246(4)	0.1232(3)	0.2413(3)	4.8
C(21)	−0.1024(5)	0.1946(5)	−0.0789(4)	7.3
C(22)	−0.0919(6)	0.1592(4)	0.0301(5)	6.3
C(23)	−0.088(1)	0.2500(0)	0.0922(6)	5.5

Table 9

Interatomic bond distances (Å) and angles (deg) for non-hydrogen atoms in (η^5-C_5H_5)(η^5-C_5Me_5)Ti(allyl) (**3**) with estimated standard deviations in parentheses

(a) Bond distance			
Ti–C(1)	2.379(9)	C(1)–C(2)	1.381(14)
Ti–C(2)	2.360(11)	C(11)–C(12)	1.423(10)
Ti–C(11)	2.426(7)	C(11)–C(16)	1.505(8)
Ti–C(12)	2.410(7)	C(12)–C(13)	1.417(10)
Ti–C(13)	2.420(7)	C(12)–C(17)	1.516(8)
Ti–C(21)	2.450(5)	C(13)–C(18)	1.503(8)
Ti–C(22)	2.396(6)	C(21)–C(22)	1.461(8)
Ti–C(23)	2.363(8)	C(22)–C(23)	1.402(9)
(b) Bond angle			
C(1)–Ti–C(1′)	62.5(3)	C(11)–C(12)–C(17)	126.3(6)
C(1)–C(2)–C(1′)	126.7(8)	C(13)–C(12)–C(17)	125.5(6)
C(12)–C(11)–C(16)	125.6(6)	C(12)–C(13)–C(18)	124.0(6)
C(11)–C(12)–C(13)	107.8(6)	C(21)–C(22)–C(23)	106.3(5)

geometries of the diene ligand changes drastically depending upon the steric interference between the substituent on the diene ligand and the ancillary C_5Me_5 ligand. Short Ti–C(1) and Ti–C(2) bonds comprise a remarkable structural feature in complex **3** (2.379 and 2.360 Å) as compared with those of **1** and **2**. The shortening of the Ti–C bonds, which obviously brings about the shortest Ti–M1 distance, should arise from the reduced steric bulkiness of the allyl ligand. As summarized in Table 7, the C(1) and C(3) atoms in the complexes **1**–**3** have close contact with the facing C(11), C(12), C(21), or C(11), C(15), C(25) atoms and C(2) carbons have close contact with C(21) and C(25) atoms. A short non-bonding distance is also observed between C(1) and C(17) (3.468 Å) in complex **3**. The shortest non-bonded contact (2.958 Å) between C(2) and C(21) atoms is found in the complex **3**. The C(1)–C(2)–C(3) angles of **2** [av. 126.8°] and **3** [126.7°] are the largest of those in allylic metal compounds.

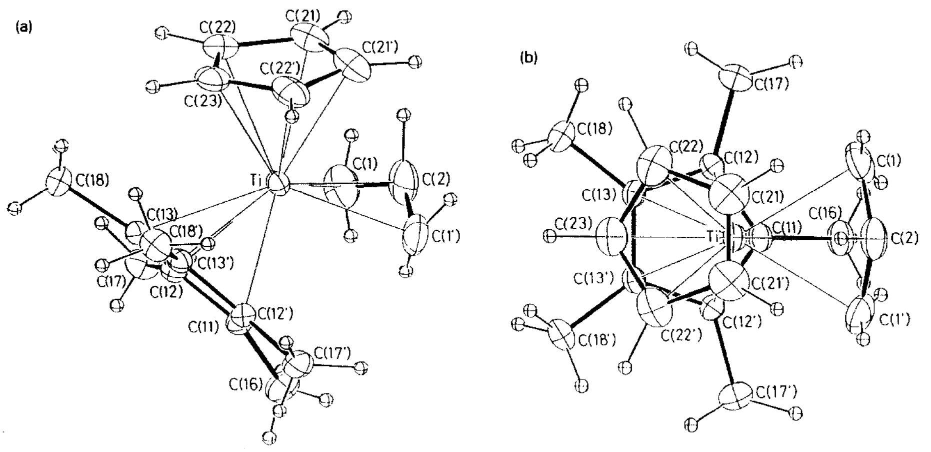


Fig. 3. Molecular structure of (C_5H_5)(C_5Me_5)Ti(allyl) (**3**) by the ORTEP drawing with the thermal ellipsoids at 20% probability level; (a) side view, and (b) top view.

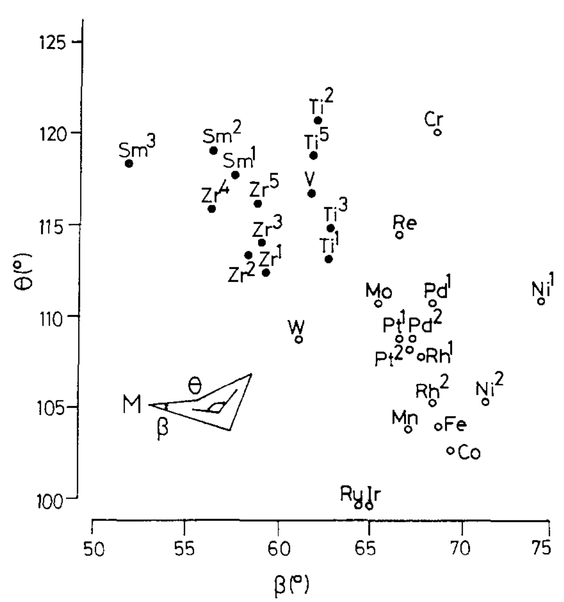


Fig. 4. Coordination geometry in the early and late transition metal-allyl complexes by the bite angle (β) vs. bent angle (θ) plotting [10]. Ti^1: $TiCp_2$(1,3-dimethylallyl), Ti^2: $TiCp_2$(2-methylallyl), Ti^3: $Ti(C_5Me_5)Cp$(allyl), Ti^5: $TiCp_2$(1,2-dimethylallyl), V: $V(CO)_3(Me_2AsC_6H_4AsMe_2)$(1-methylallyl), Zr^1: $Zr(C_5Me_5)(C_8H_8)$(allyl), Zr^2: $Zr(C_8H_8)(OBu^t)$(allyl), Zr^3: $Zr(C_5Me_5)Br_2$(1,2,3-trimethylallyl, Zr^4: $ZrCp_2Br$(1,2,3-trimethylallyl), Zr^5: $Zr(C_5Me_5)Br_2$(1,1,2-trimethylallyl), Sm^1: $Sm(C_5Me_5)_2$(allyl), Sm^2: $Sm(C_5Me_5)_2$(1-methylallyl), Sm^3: $Sm(C_5Me_5)$(1-phenylallyl)(OC_8H_8), Cr: $Cr_2(allyl)_4$, Mn: $Mn(CO)_2[P(OMe)_3]$(allyl), Fe: $[Fe(CO)_3(allyl)]_2$, Co: $Co(CO)_2PPh_3$(allyl), $Ni^{1,2}$: $Ni(allyl)_2$, Mo: $MoCp(allyl)_2$, Ru: $Ru(NO)(PPh_3)$(allyl), Rh^1: $Rh(PHCy_2)_2$(2-methylallyl), Rh^2: $Rh(C_5Me_5)Cl$(1,3-dimethylallyl), Pd^1: $Pd(C_6H_7N)Cl$(1,2-dimethylallyl), Pd^2: Pd_3Cl_4(2-methylallyl)$_2$, W: WCpI(NO)(allyl), Re: $Re_2(allyl)_4$, Ir: $Ir(1,5\text{-}C_8H_{12})[P(OMe)_3]$(allyl), $Pt^{1,2}$: $Pt(C_4H_8)(PPh_3)$(2-methylallyl)PF_6.

Structural characteristics in allyl compounds of early transition metals. Although allylic metal compounds of late transition metals as well as early transition metals are ubiquitous, crystallographic studies of titanium compounds are still rare. A geometrical comparison of the present allyltitanium compounds with the other early transition metal- and late transition metal-allyl compounds can be made from Fig. 4, a β vs. θ plot. The relatively smaller bite angle, β, and larger bent angle, θ, for the early transition metal complexes compared with those for Pt, Pd, Fe, Rh analogues can be clearly seen. The β angles for early transition metal compounds appear in a narrow range, 51.7–62.5°, the value being remarkably smaller than those (66–72°) observed for $[Pt(C_4H_8)(PPh_3)$(2-methylallyl)] ($Pt^{1,2}$ in Fig. 4), $Pd(C_6H_7N)Cl$(1,2-dimethylallyl)(Pd^1), Pd_3Cl_4(2-methylallyl)(Pd^2), $Rh(C_5Me_5)Cl$-(1,3-dimethylallyl) (Rh^2) and Ni(allyl) ($Ni^{1,2}$). This difference cannot be correlated directly to the magnitude of the ionic radius of the metal but is largely effected by the π-accepting property of the metal. The θ values for complexes **1**–**3** as well as those for other titanium, zirconium, vanadium, and samarium complexes all fall in the same range, 112.0–121.5°, e.g. $Zr(C_5Me_5)(C_8H_8)$(allyl) (112.6°, Zr^1 in Fig. 4), $Zr(C_8H_8)(O^tBu)$(allyl) (113.5°, Zr^2), $Zr(C_5H_5)_2Br$(1,2,3-trimethylallyl) (116.3°, Zr^4), $Sm(C_5Me_5)_2$(ally) (116.4°, Sm^1), $Sm(C_5Me_5)_2$(1-methylallyl) (119.1°, Sm^2), while those for late transition metals usually have smaller values (99.5–111.1°).

$TiCp_2$(2-methylallyl) (**2**) exhibits the largest θ value while those for the corresponding 2-methylallyl compounds of Pt, Pd, and Rh take much smaller values of 108.4° (av. of Pt^1 and Pt^2 in Fig. 4), 109.1° (Pd^2) and 108.3 (Rh^1), respectively. Therefore, the smaller θ values for these late transition metals are ascribed to their stronger π-accepting property. In general, early transition metal compounds have longer M–C(1) and M–C(2) distances (2.38–2.49 Å) than the late transition metal compounds (1.98–2.29 Å) which correlate to the density of the substituent on the allyl ligand and the metal. The differences in bond lengths defined by [(M–C(1)) + (M–C(3))]/2–(M–C(2)) range from −0.08 to 0.03 Å for the early transition metals whereas for the late transition metal compounds values are larger (0.05–0.14 Å) in support of above description regarding the magnitude of the θ values.

Supplementary Material. The following tables are available from Y. Kai: Listings of anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for hydrogen atoms with isotropic temperature factors, and bond distances and angles including hydrogen atoms of complexes **1**, **2**, and **3**; atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms, and bond distances and angles of complex **4**; listings of observed and calculated structure factors for complexes **1**, **2**, and **3**.

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9 Crystal data of $(C_5H_5)_2$Ti(allyl) (**4**) and $(C_5H_5)_2$Ti(1-methylallyl) (**6**). **4**: $C_{13}H_{15}Ti$, FW = 219.2, monoclinic, space group $C2/c$ or Cc, at 20 °C, $a = 13.319(3)$, $b = 7.618(1)$, $c = 11.982(3)$ Å, $\beta = 114.55(2)°$, $V = 1105.9(4)$ Å^3, $Z = 4$, $D_c = 1.316$ g cm^{-3}, $F(000) = 460$, μ(Mo-K_α) = 7.4 cm^{-1}; **6**: $C_{14}H_{16}Ti$, FW = 232.2, monoclinic, space group $C2/c$ or Cc, at 20 °C, $a = 13.350(5)$, $b = 7.719(1)$, $c = 12.887(5)$ Å, $\beta = 112.32(3)°$, $V = 1228.6(7)$ Å^3, $Z = 4$, $D_c = 1.255$ g cm^{-3}, $F(000) = 488$, μ(Mo-K_α) = 6.8 cm^{-1}. The molecular structure of complex **4** is regarded as the most important in this series of allyltitanium complexes to get the fundamental geometrical parameters of the allyl coordination to Ti atom. Thus, the crystal structure study of **4** was extensively carried out including the repeated recrystallizations and intensity measurements. The thermal ellipsoids even in the best molecular structure of **4** obtained hitherto for the putative space group of Cc includes the abnormal size and anisotropy for the apparent thermal vibrations of the atoms, particularly the central carbon atom of the allyl ligand. The structure might be the result of fluxional coordination properties of the cyclopentadienyl and the allyl ligands to the titanium atom. Therefore, only limited discussion of the

molecular structure is possible. The R index is 0.099 for the 1167 observed reflections [$|F_o| > 3\sigma(F_o)$] of the 1614 measured. The molecular structure of **6** was also expected to reveal the substituent effect on the asymmetrical position of allyl ligand. The structural determination of **6** presented the same difficulties as those met for **4**. The mixed ancillary ligand complexes of $(C_5H_5)(C_5Me_5)$Ti(1-methylallyl), was also repeatedly prepared and crystallized to find some breakthrough in the structure determination of (asymmetrically substituted allyl)titanium complex, but the crystals obtained hitherto were not suitable for X-ray crystallography. Although repeated crystallizations of **5** were carried out in an attempt to obtain a new form of crystal by varying the conditions of crystallization only the same crystal form as that reported by Helmholdt et al. [6] was obtained.

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